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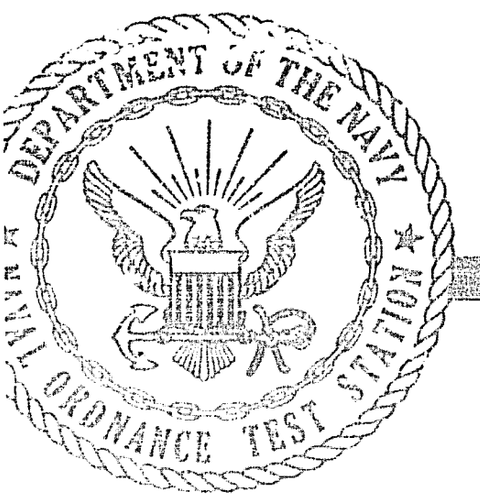

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NOTS TP 1997 NAVORD REPORT 5870

NUMERICAL EVALUATION OF SUPERRATE BURNING OF EXTRUDED DOUBLE-BASE PROPELLANTS AND THE RELATED IMPORTANCE OF THE CHEMICAL STRUCTURE OF BURNING-RATE MODIFIERS (C)

By

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FOREWORD

This report is based on studies conducted with ballistic modifiers for double-base propellants since 1947, principally at the Allegany Ballistics Laboratory and the Naval Ordnance Test Station. Much of the work has been presented in progress reports and papers issuing from both activities since 1950. The present report is an attempt to consolidate this information and to present an analysis of it in a newly organized form. The approach and treatment differ from those of earlier reports in being more highly specialized. The purpose has been to elucidate the reaction mechanisms of many lead compounds in double-base propellants with the help of a numerical analysis of their burning-rate accelerating effects and to define the important elements of their chemical structures as these appear to be related to their effects in propellants.

The work was performed under various Bureau of Ordnance Task Assignments and with Exploratory and Foundational funds.

This report is transmitted for information only and does not necessarily represent the official views or final judgment of this Station.

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ABSTRACT

A mathematical analysis was made of the burning rate accelerating effect of numerous lead compounds in extruded double-base propellants. This study showed the generally greater rate accelerating effect of hydroxy or similarly substituted aromatic lead compounds relative to the aliphatics, especially in the presence of other substituents which allow formation of bidentate groups. These groups seem to activate the aromatic nuclei for electrophilic substitution and to preserve the reactivity of the lead in the preparation zone of the solid propellant decomposition wave. In some cases, deactivation by further substituents and over-protection by intramolecular resonance have been observed or inferred. References are made to other reports which deal with the possible mechanism involved in this form of double-base propellant burning.

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Tables:

INTRODUCTION

The burning rates of some double-base propellants containing certain lead compounds exceed very significantly the burning rates of lead-free propellants in certain pressure ranges. Within these ranges leaded propellants exhibit, at low pressures, high pressure exponents[1] which are followed, at increased pressure, by relatively low, zero, and sometimes negative pressure exponents.

In a systematic approach begun several years ago, a series of lead compounds of organic materials was investigated. This study quickly indicated the possibility of a definable relationship between chemical constitution and "modifier effectivity". Further work has led to a clearer and more quantitative understanding of the so-called "mesa" and "plateau" effects in the burning-rate-pressure relationship. The synergistic effects of mixtures of lead and copper compounds are not covered in the present report even though they are exceedingly useful in present-day service propellants such as X-12, X-13 and X-14 compositions developed at the Naval Ordnance Test Station. Here the effects would appear to require more study before a meaningful analysis can be attempted.

COMPARISON OF LEAD COMPOUNDS BY "MODIFIER EFFECTIVITIES"

In Ref. 1 an attempt was made to introduce a numerical evaluation into the discussion of the influence of additives which produce plateau or mesa burning of double-base propellants. As an early yardstick for the quantification, the maximum increase of the burning rate produced by the additive was used. This increase had earlier been called "superrate burning" (Ref. 2). A still more powerful measure of the effect could be represented on the burning rate diagram by an area which is enclosed by the rate-pressure isotherms of the propellant containing the additive and the propellant without such additive. Typical forms of such

[1] The pressure exponent is the value of "n" in the equation $r = cP^n$ where "r" is the linear burning rate, "c" is a constant at any temperature and "P" is the chamber pressure during combustion.

graphs are shown in Fig. 1. (The compositions of these propellants are given in Table 1.) These lines are substantially convergent at low pressure (50 to 800 psi), separate at a pressure which is highly dependent on the structure of the lead compound, and essentially unite again at higher pressures. The burning rate-pressure-temperature data from strand burning tests are normally plotted on log-log graphs for ease in the determination of pressure exponents and temperature coefficients. For the purpose of a numerical evaluation, it appeared desirable to evaluate these "superrate areas" by integrating them in linear coordinates, not in logarithmic ones. In Ref. 1, this new method for evaluating the burning rate diagrams has been described as follows:

"The areas bounded by the curved rate-pressure plot (for 70°F testing) and a straight line of slope (pressure exponent) equal to 0.7 coinciding with the high and low pressure portions of each plot in logarithmic coordinates have been converted to linear coordinates and integrated with the aid of IBM equipment. Areas are in the dimensions of

$$\frac{\text{pounds (force)}}{\text{inch}^2} \cdot \frac{\text{inch}}{\text{sec}} = \frac{\text{pounds (force)}}{\text{inch}} \cdot \frac{}{\text{sec}}$$

While these units may have no particular physical significance, a comparison of these values of area at constant concentration of lead compounds may presumably offer a fair indication of the relative catalytic effect of various compounds." In those few cases where available data did not show convergence of the superrate diagram and the base line, the area was closed arbitrarily by extrapolating the diagram to meet the base line. Data were almost invariably carried at least to the point where the low pressure end of the superrate diagram was dropping sharply toward the base line. The selection of a 0.7 value for the slope of the base line was arbitrary; it was also conservative since it tended to minimize the enclosed area of superrate burning. Some unmodified double-base systems show slopes closer to unity.

In a later consideration of these figures, it was observed that better results were obtained if propellants having similar heats of explosions were compared. How much the data are changed by a change in the heat of explosion can be seen by comparing PL 120 and PL 220[2] which have similar composition and

[2] Designation of experimental propellant lots in the monthly progress reports by the Propellants Division of NOTS.

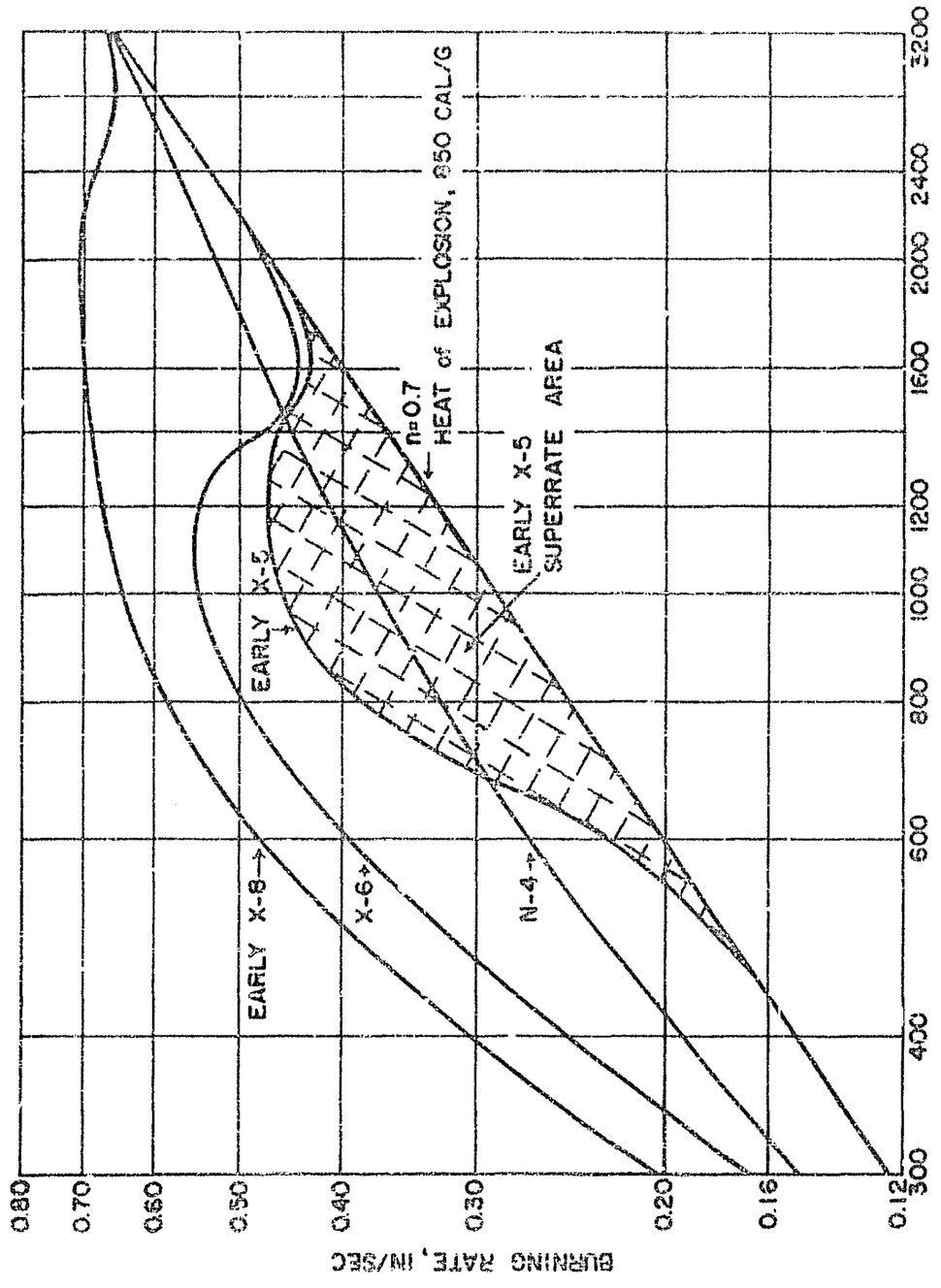


FIG. 1. Superrate Areas of Typical Propellant Compositions (See Table).

TABLE 1. Composition and Heat of Explosion of Propellants Shown in Figure 1.

Composition and heat of explosion	N-4[a]	Early X-5[b]	X-6[c]	Early X-8[d]
A. Basic Compositions, Weight, %				
Nitrocellulose, 12.6% N	54.0	52.0	49.0	50.0
Nitroglycerin	31.6	33.1	35.5	34.2
Diethyl phthalate	10.1	10.9	9.3	9.8
2-Nitrodiphenylamine	2.0	2.0	2.0	2.0
B. Modifiers, Weight, %				
Potassium sulfate	1.5	....	....	....
Carbon black	0.1	....	....	....
Lead stearate	0.5	....	....	....
Lead salicylate	....	1.3	3.0	2.0
Lead 2-ethylhexanoate	....	0.7	1.2	....
Lead β-resorcylate	....	....	....	2.0
C. Heat of Explosion, Q				
Measured, cal/g	856	864	848	820

[a] Lot PAE-138, Reference NOTS Report No. TM 469.

[b] PL 167, Reference NOTS Report No. TM 456.

[c] Lot PAE-6130, Reference NOTS Report No. TM 1048.

[d] PL 419, Reference NOTS Report No. TM 1096.

constituents except for the higher ratio of nitroglycerin to plasticizer in PL 220.

TABLE 2. Influence of a Change in Heat of Explosion on the Superrate of Similar Double-base Propellants

Properties	PL 121	PL 220
Heat of explosion, cal/g	770	866
Total area of superrate	250	175
Lead salicylate, %	2.0	2.3

This sensitivity to heat of explosion was already well known and had led to the assumption that the plateau or mesa effect might exist only below a certain combustion gas temperature at which the gas composition was nearly independent of the pressure (Ref. 3). With increasing flame temperature and heat of explosion, the influence of lead compounds would therefore decrease. More recent results with improved lead compounds have shown that it is possible to obtain plateau effects with high energy propellants whose flame temperatures would indicate appreciable dependence of gas composition on pressure. Combinations of lead compounds and copper compounds extend these possibilities still further. However, the characteristic decrease of the "superrate area" with increasing heat of explosion is still apparent, and this effect makes it necessary to compare data from different propellants on the basis of equal, or at least very similar, heats of explosion.

A large variety of changes can be made to alter the properties of an extruded double-base propellant. Besides changes in the ratio of nitroglycerin to nitrocellulose, changes in the nature and content of the stabilizer, plasticizer, high explosive additives, or metal compounds, can influence burning properties. In the studies upon which much of the present analysis is based, the range in composition was kept small except for the ratio of nitroglycerin to plasticizer and the nature and content of the lead compounds to be tested, as Table 3 indicates:

TABLE 3. Range of Composition of Double-Base Propellants Used in the Present Evaluation

Ingredients	Percent by weight
Nitrocellulose, 12.6% N	50.0 - 2
Nitroglycerin	35.0 - 6
Diethyl phthalate or di-n-propyl adipate ...	8.0 - 5
2-Nitrodiphenylamine	2.0 - 0.5
Lead compounds	2 to 3
Heat of explosion, cal/g	720 to 1050

The results of these studies were useful in showing, for a given energy level, the relative influences of a large number of lead compounds on the burning rate. One purpose of this comparison was to find guide lines for further improvement of such compounds, even without establishing the reaction mechanism involved, by comparing the structure of the additive with the results obtained.

For the initial comparison of the effects of the added lead compounds, the quotient of the "superrate area" divided by the weight fraction of the lead compounds contained in the propellant had been used (Ref. 1). However, since the molecular weights of such compounds and the percentage of metal therein tended to vary widely, it appeared advisable to divide the superrate area by the easily determined, weight percent of lead in the propellants. This quotient is called "modifier effectivity". Derived from an area, its value is dependent as much on sustained rate-boosting effects of a modifier as it is on a more marked effect which might occur over a smaller pressure range. Since the burning-rate-modifying agents were generally well defined chemical compounds of lead with organic groups, a definite stoichiometric relationship existed between these parts of the molecule.

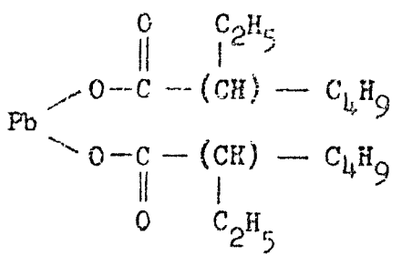
The assumption had to be made of course that such division of the "superrate area" by lead metal contents would give, even at different levels of lead content, sufficiently comparable data. For this reason, the percentage of lead compounds was adjusted in these investigations to give reasonably uniform lead metal contents where large differences existed in the molecular weights of the additives. For small variations of the molecular weights, it was assumed that proportionality existed between the changes of the "superrate area" and the lead content for a given propellant composition.

The weight percentage of lead compounds used in these compositions was based largely on previous studies by the Allegany Ballistics Laboratory (ABL) and by the U. S. Naval Ordnance Test Station (NOTS) concerning the form of such "superrate areas" (Ref. 1, 4, and 5). The actual shape of such areas was neglected in the present search for a practical evaluation tool.

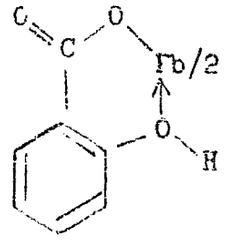
In the following part of this report an attempt is made to apply the evaluation method, based on "modifier effectivity", to practical double-base propellants most of which were prepared as a part of a broader applied research and development program.

RESULTS OF THE APPLICATION OF THE ABOVE METHOD

Influences of Lead Salicylate and Related Compounds. In this investigation of constitutional influences, the different burning-rate-modifying agents were compared in propellants having about the same heats of explosion. "Modifier effectivities" were calculated from the integrals of the "superrate area" by dividing this area by the metal content of the propellant. Table 4 shows such a comparison between lead 2-ethylhexanoate and lead salicylate. Similar results were obtained in a comparison of lead salicylate and other lead salts of aliphatic acids, such as lead stearate.



1. Lead 2-ethylhexanoate



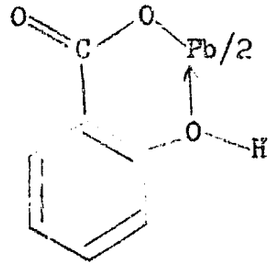
2. Lead salicylate (Lead 2-hydroxybenzoate)

TABLE 4. Comparison of Lead 2-ethylhexanoate and Lead Salicylate as Burning Rate Modifiers

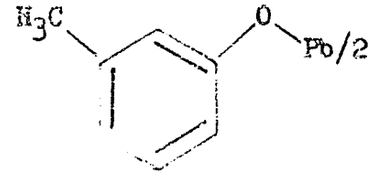
Characteristics	1. Pb 2-ethyl-hexanoate	2. Pb salicylate
Modifier effectivity	66	291
Superrate area	44	250
Pb compound by analysis, %	1.6	2.0
Pb in compound, %	41.98	43.04
Pb in propellant, %	0.67	0.86
Heat of explosion of propellant, cal/g	784	770
PL No	121	120

It can be seen that large differences exist in the "modifier effectivity" between compound 1 and 2; the salicylate used in the second composition being more than four times as effective as the ethylhexanoate in the first compound.

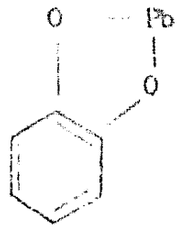
The question arose as to which constitutional differences between the two lead compounds might be related to the above dissimilarities in "modifier effectivity." Both compounds are salts of carboxylic acids and do not ionize extensively; even lead acetate in dilute aqueous solutions shows a small degree of dissociation (Ref. 6), and complex ions are formed in concentrated solutions (Ref. 7 and 8). The exchange of an aliphatic carboxylic acid by an aromatic carboxylic acid does not change such properties very greatly. In comparable double-base propellants, the Allegany Ballistics Laboratory (ABL) found a very similar behavior of lead 2-ethylhexanoate and lead ortho-toluate up to 2,000 psi (Ref. 9). Therefore, other reasons had to be found for the differences between the effectivities of the lead salts of these two acids. The only other difference between lead ethylhexanoate and lead salicylate is the presence of a phenolic hydroxyl group which makes the aromatic nucleus highly subject to electrophilic attack. Thus it was necessary to investigate such influence with compounds which could show their contribution separately from other effects. For this purpose, the data for lead m-cresolate and lead catecholate have been compared with data for lead salicylate as similar heats of explosion as shown in Table 5. For comparison with lead catecholate, basic lead salicylate with similar lead content has been used.



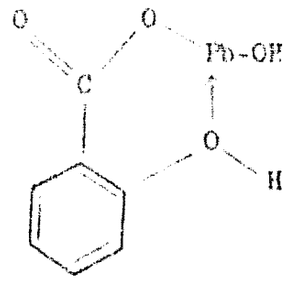
2. Lead salicylate



3. Lead m-cresolate



5. Lead catecholate

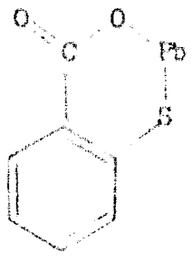


6. Basic lead salicylate

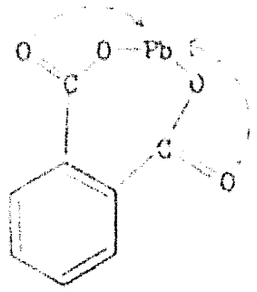
TABLE 5. Influence of Phenolic Hydroxyl Groups in the Absence of Carboxyl Groups

Characteristics	2. Pb salicylate	3. Pb m-cresolate	5. Pb catecholate	6. Basic Pb salicylate
Modifier effectivity	291	20	26	198
Superrate area	250	29	49	231
Pb compound by analysis, %	2.0	3.1	2.9	2.0
Pb in compound, %	43.04	45.69	65.72	58.81
Pb in propellant, %	0.86	1.41	1.90	1.17
Heat of explosion of propellant, cal/g	770	763	863	880
PL No.....	120	422	644	ABL2318

It may be concluded that neither the aromatic carboxyl group as present in lead ortho-toluate nor the phenolic hydroxyl of the aromatic acid by itself produces lead salts with such high "modifier effectivity". It followed that the presence of both of these groups in the lead salts in proper relative position might be necessary. For examination of this possibility, it appeared desirable to determine whether or not the hydroxyl group of salicylic acid could be replaced with other groups of similar electrical influence without greatly influencing the "modifier effectivity" of the lead salts. For this purpose, data of the Allegany Ballistics Laboratory (ABL) about basic lead salicylate and lead thiosalicylate (Ref. 9) could be used to supplement local information.



7. Lead thiosalicylate



8. Lead phthalate

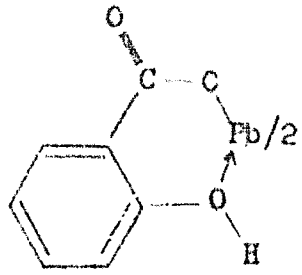
TABLE 6. Influence of an Exchange of the Ortho Hydroxyl Group of Basic Lead Salicylate by Other Groups

Characteristics	6. Basic Pb salicylate	7. Pb thiosalicylate	8. Pb phthalate	1. Pb 2-ethylhexanoate
Modifier effectivity	198	148	101	66
Superrate area	231	170	104	44
Pb compound by analysis, %	2.0	2.0	2.0	1.6
Pb in compound, %	58.81	57.66	51.38	41.98
Pb in propellant, %	1.17	1.15	1.03	0.67
Heat of explosion of propellant, cal/g	880	880	757	784
PL No	ABL2318	ABL2070	266	121

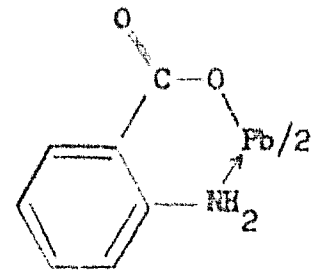
For comparison with lead thiosalicylate it was necessary to use basic lead salicylate which contains a very similar amount of lead (see Table 6). Lead phthalate also has a comparable lead content, since the ortho hydroxyl group of lead salicylate has been replaced by a second carboxyl group. The relative "modifier effectivities" were 74.7% for lead thiosalicylate and 51% for lead phthalate when compared with that of basic lead salicylate. Compared to lead 2-ethylhexanoate, the effectivity of lead phthalate was 151%. These relatively high data are surprising since phthalic acid itself is very stable against electrophilic attack. The difference may be due to a form of improved protection of the lead ion through steric influences similar to the presence of bidentate groups in

the organic part of the burning rate modifier. This expression, of course, indicates "two-toothed" chemical compounds which are able to form chelates.

For evaluation of the properties of lead anthranilate, a propellant containing the normal salt of lead salicylate was again used as a reference. Table 7 shows the data for the performance of these propellants.



2. Lead salicylate



4. Lead anthranilate

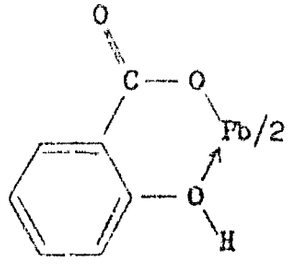
TABLE 7. Influence of an Exchange of the Ortho Hydroxyl Group of Normal Lead Salicylate by an Amino Group

Characteristics	2. Pb salicylate	4. Pb anthranilate	1. Pb 2-ethylhexanoate
Modifier effectivity	291	140	66
Superrate area	250	181	44
Pb compound by analysis, %	2.0	3.0	1.6
Pb in compound, %	43.04	43.22	41.98
Pb in propellant, %	0.86	1.30	0.67
Heat of explosion of propellant, cal/g	770	773	784
PL No	120	490	121

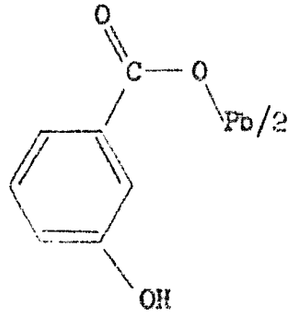
The datum obtained for lead anthranilate was 48.1% that of lead salicylate but would probably have been somewhat higher if lead anthranilate had been used in the same concentration as lead salicylate. The value is still 212% of the datum for lead 2-ethylhexanoate and indicates the same tendency of bidentate groups to increase the effectivity of aromatic compounds. The conclusion that the increased performance may be due to bidentate

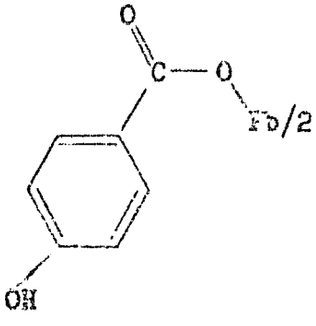
groups needed to be checked by comparison with isomeric compounds having substituents in other than the bidentate position.

L. Pauling observes in Ref. 10 that neither 3- nor 4-hydroxybenzoic acid forms intramolecular hydrogen-bonded chelates, whereas salicylic acid forms such compounds easily. A comparison of the corresponding lead salts was, therefore, made and Table 8 shows the results of this evaluation.



2. Lead salicylate
(Lead 2-hydroxybenzoate)





9. Lead 3-hydroxybenzoate 10. Lead 4-hydroxybenzoate

TABLE 8. Influence of the Position of the Hydroxyl Group in Lead Hydroxybenzoates

Characteristics	2. Pb salicylate	9. Pb 3-hydroxybenzoate	10. Pb 4-hydroxybenzoate	1. Pb 2-ethylhexanoate
Modifier effectivity ...	291	148	154	66
Superrate area	250	140	126	44
Pb compound by analysis, %	2.0	2.2	1.8	1.6
Pb in compound, %	43.04	43.04	43.04	41.98
Pb in propellant, %	0.86	0.94	0.82	0.67
Heat of explosion of propellant, cal/g	770	774	764	784
PL No.	120	243	217	121

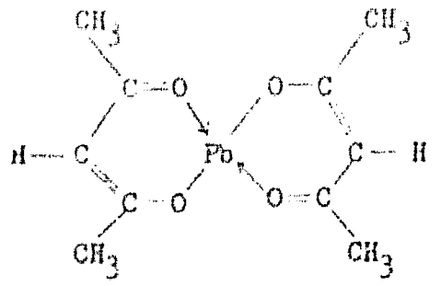
The lead salicylate is about twice as effective as the 3- and 4-hydroxybenzoates. This supports the previously mentioned indication of better performance of compounds containing bidentate groups. Another interesting result is that both the 3- and 4-hydroxybenzoates give considerably higher "modifier effectivities" than lead 2-ethylhexanonate in spite of the minor results obtained with lead salts of compounds containing phenolic hydroxyl groups but no carboxyl groups. Such compounds were shown in Table 5 as lead m-cresolate (No. 3) and lead catecholate (No. 5).

The superior results of lead salicylate demanded a continutation of the present investigations predominantly in the direction of compounds containing bidentate groups.

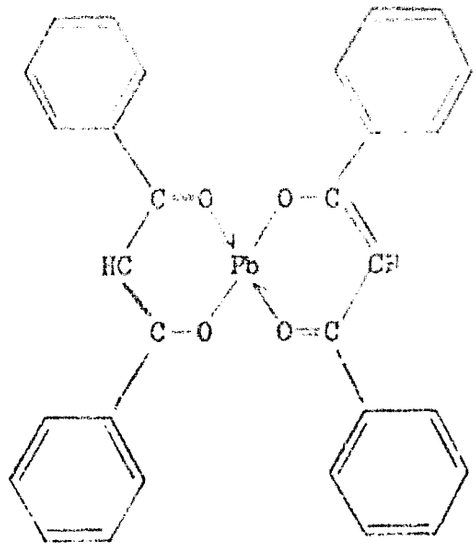
Inflences of Non-Aromatic or Aromatic-Substituted Aliphatic Bidentate Groups. The assumption that bidentate arrangement of substituents might be of advantage for production of high "modifier effectivities" had been made on the basis of relatively few experiments. It thus appeared necessary to determine whether bidentate groups in general would show similar relationships, or if only a small group of such compounds would act similarly.

Accordingly, it appeared necessary to separate the effects of aromatic bidentate groups and bidentate groups. The Allegany Ballistics Laboratory (ABL) already had investigated two lead salts of organic compounds containing aliphatic bidentate groups (Ref. 11). The results of these investigations showed, in the first case, that lead lactate produced only minor effects which were similar to those of lead acetate (Ref. 5). In the second case, lead acetylacetonate gave similarly small effects. For this reason, an attempt was made to compare lead salicylate with lead salts of compounds which would be more nearly like salicylic acid than acetylacetone which is enolized only to about 76%. Such a compound, which exists almost exclusively in the enol form is dibenzoylmethane (Ref. 12).

The lead salt of dibenzoylmethane furthermore had the advantage that the aromatic nuclei of this compound were very stable toward any substituting influences. For instance, the rings would be much less reactive than those of the lead salts of 3- and 4-hydroxybenzoic acids. The results of this investigation are shown in Table 9.



11. Lead acetylacetonate



12. Lead dibenzoylmethane

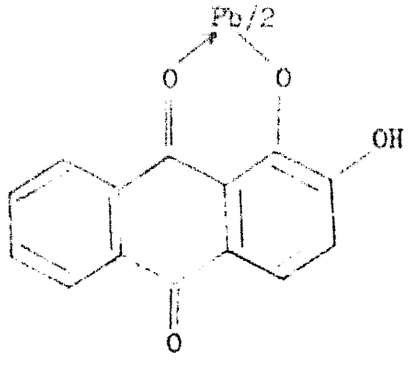
TABLE 9. Influence of Bidentate Groups in the Absence of Reactive Aromatic Nuclei

Characteristics	12. Pb dibenzoylmethane	13. Pb salicylate
Modifier effectivity	10	156
Superrate area	12	195
Pb compound by analysis, %	3.8	2.2
Pb in compound, %	31.6	43.44
Pb in propellant, %	1.2	1.25
Heat of explosion of propellant, cal/g	830	868
PL No	645	227

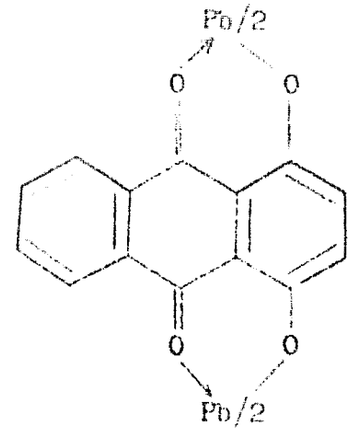
These data show that the presence of bidentate groups in the lead compound does not, by itself, produce any increase in the burning rate of the propellant. Therefore, the conclusion appeared reasonable that only the same functional bidentate groups containing a phenolic hydroxyl group or its equivalent could produce burning rate modifying effects similar to those of lead salicylates.

Influences of Aromatic Carbonyl Compounds Containing Phenolic Hydroxyl Groups in Bidentate Positions. It appeared necessary to

test the above conclusion by replacing the carboxyl groups with carbonyl compounds of the aldehyde, keto, or quinone group series. A phenolic hydroxyl group in vicinal position to each of the above groups were used in order to produce a bidentate group. Alizarin and quinizarin were selected for preparation of lead salts because of their good availability and because they seemed to fulfill the above requirements, see Table 10.



14. Lead alizarinate



15. Lead quinizarinate

TABLE 10. Influence of Aromatic Carbonyl Compounds With Bidentate-Forming Hydroxyl Groups

Characteristics	14. Pb alizarinate[a]	15. Pb quinizarinate[b]	13. Pb salicylate	26. Pb β-resorcylate[c]
Modifier effectivity ...	395	75	156	382
Superrate area	237	132	195	340
Pb compound by analysis, %	2.0	3.8	2.9	2.2
Pb in compound, %	30.2	46.5	43.04	40.36
Pb in propellant, %	0.60	1.76	1.25	0.89
Heat of explosion of propellant, cal/g	858	852	868	839
PL No	590	642	227	392

[a] Prepared by reaction in aqueous solution of two moles of monosodium alizarinate with one mole of lead nitrate. Memo P4011-140 to Code 4021, 11 August 1953, CONFIDENTIAL.

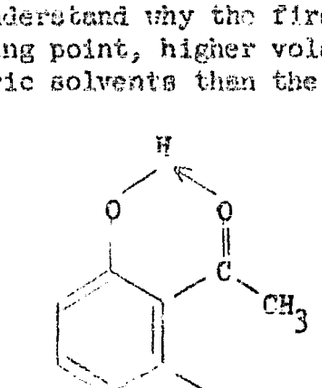
[b] Prepared by reaction in aqueous solution of disodium quinizarinate with molecular amounts of lead acetate. Memo P4011-147 to Code 4021, 27 October 1953, CONFIDENTIAL.

[c] See page 25.

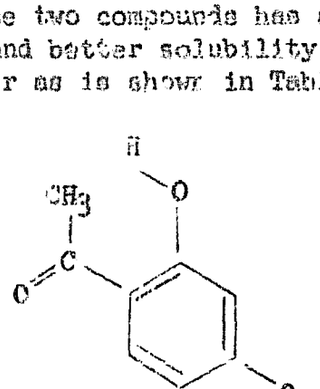
The "modifier effectivity" of lead alizarinate, in which only one quinone oxygen may form a chelate complex, is very high — considerably higher than that of lead salicylate. It is approached only by No. 26, lead β-resorcylate, which also contains an additional hydroxyl group like lead alizarinate. This result shows that if chelation is important, a coordination involving an aromatic hydroxyl and a carboxyl group.

The results obtained with lead quinizarinate are much lower than those obtained with lead alizarinate and require further special consideration because lead quinizarinate shows only half of the "modifier effectivity" of lead salicylate. This decrease is larger than that which might be expected as a result of the absence of any hydroxyl group outside the bidentate groups. The two possible chelate groups in the molecule of lead quinizarinate may be largely affected by intramolecular resonance. Such effects can sometimes become so strong that the normal reactions of the metal atoms are eliminated and the intermolecular relationships of such molecules are decreased (Ref. 13).

Closely related isomeric compounds show striking differences in boiling and melting points because of intramolecular relationships and resonance effects. The double chelates of 2,4- and 4,6-diacetylresorcinol were discussed in Ref. 10 from the viewpoint of fixation of Kekulé structures favoring double hydrogen bonds for the 2,4 compound but only single hydrogen bonds for the 4,6 isomer. This theory of intramolecular bonding was necessary to understand why the first of these two compounds has a lower melting point, higher volatility, and better solubility in non-polaric solvents than the 4,6 isomer as is shown in Table II.



2,4-Diacetylresorcinol

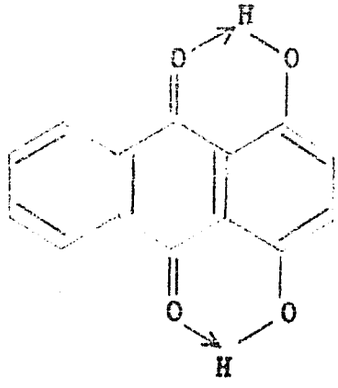


4,6-Diacetylresorcinol

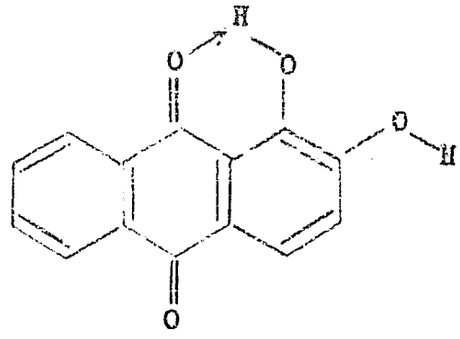
TABLE 11. Physical Properties of Dihydroxy Diketones With Different Degrees of Chelation

Properties	2,4-Diacetyl-resorcinol	4,6-Diacetyl-resorcinol
Melting point, °C	89	182
Volatility in steam	Easily volatile	Almost non-volatile
Solubility in benzene at 15°C, %	10	1

The above results, then, allow tentative conclusions to be made about an analogous behavior of alizarin and quinizarin compounds. Quinizarin would form an intramolecularly saturated hydrogen-bonded double chelate in a closely related manner to 2,4-diacetylresorcinol whereas alizarin would form a single chelate with considerable possibility for intermolecular association because of the remote position of the second hydroxyl group relative to the second ketone group. Table 12 shows the relationships of the physical properties of these compounds which are highly analogous to those of the diacetylresorcinols.



Quinizarin



Alizarin

TABLE 12. Physical Properties of Dihydroxy Diketones of Different Chelation Possibilities

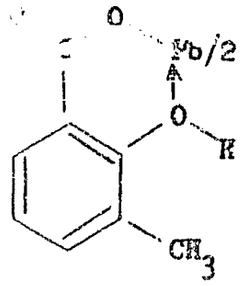
Properties	Quinizarin	Alizarin
Melting point, °C	194-5	290
Boiling point, °C	Sublimes below 195°	430
Solubility in alcohol .	Soluble	Very soluble

The changed order of the solubility data in benzene (Table 12) and in alcohol (Table 12) is due to the change from a hydrocarbon to a hydroxyl type solvent; the latter case compares more closely to the behavior in a double-base propellant matrix.

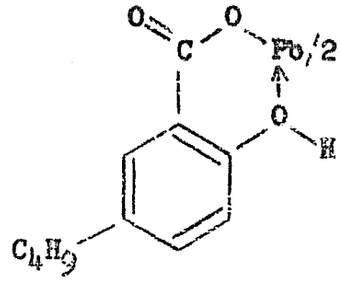
Influences of Substitution in the 3 and 5 Positions of Lead Salicylate. A tentative conclusion might be drawn at this point regarding the constitutional requirements for the organic part of those lead compounds which will have high effectivity in double-base propellants. This is, that any compound containing a bidentate group which includes an aromatic hydroxyl, mercaptan, or amino group and a carboxyl, carbonyl or equivalent group can be used to produce lead compounds of increased "modifier effectivity". This influence may be decreased if the lead-free compound shows excessive intramolecular stabilization influences. The orgenic part of the modifier seems, for this reason, to contribute considerably to the burning rate increasing effects. Whether or not this influence is due to chemical reactions involving an attack on the aromatic ring should be readily ascertainable by determining the "modifier effectivity" of compounds having appropriate groups in one or both of the reactive positions of the aromatic nucleus which are ortho and para to the hydroxyl, mercapto, or amino groups.

For this purpose, data could be used which had been obtained in earlier investigations of lead o-cresotinate and lead 5-tertiary-butylsalicylate. In lead o-cresotinate, a methyl group is present in the position ortho to the hydroxyl group. In lead 5-tertiary-butylsalicylate, the position ortho to the hydroxyl group is free, but the para group is blocked by a tertiary butyl group.

Table 13 shows the constitution of the different compounds and the results obtained.



16. Lead salt of 2-hydroxy-3-methylbenzoic acid (Lead o-cresotinate)



17. Lead 5-tertiary-butylsalicylate

TABLE 13. Influence of Substitution of the 3 or 5 Position of Hydroxybenzoic Acids

Characteritics	Low heat of explosion			High heat of explosion	
	16. Pb o-cresotinate	2. Pb salicylate	1. Pb 2-ethylhexanoate	17. Pb 5-tertiary-butyl salicylate	13. Pb salicylate
Modifier effectivity	97	291	66	193	156
Superrate area	126	250	44	195	199
Pb compound by analysis, %	3.2	2.0	1.6	2.9	2.9
Pb in compound, %	40.64	43.04	41.98	34.92	43.84
Pb in propellant, %	1.3	0.85	0.67	1.01	1.25
Heat of explosion of propellant, cal/g	748	770	784	842	868
PL No	486	120	121	683	227

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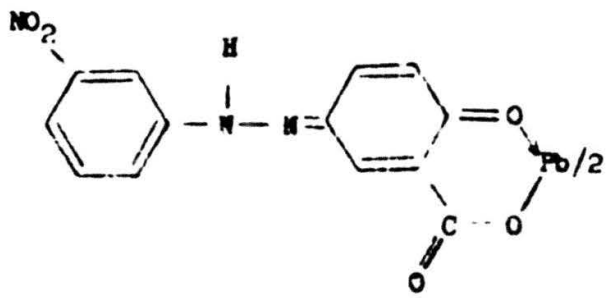
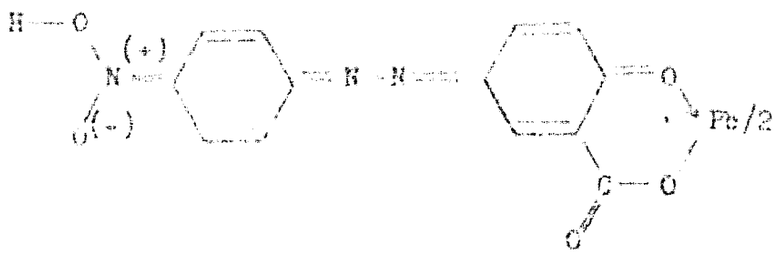
With the introduction of the methyl group in the 3 position, as in lead o-cresotinate (No. 16), the "modifier effectivity" drops to about one-third of that of lead salicylate but is still 50% better than the datum for lead 2-ethylhexanoate. The data for lead 5-tertiary-butylsalicylate show that substitution in the 5 position does not change the effectiveness of lead salicylate very markedly. The apparent, moderate superiority of the lead 5-tertiary-butylsalicylate may be due merely to the lower heat of explosion of this lot relative to the No. 13 lead salicylate control lot. It may also be due in part to the observed solubility of lead 5-tertiary-butylsalicylate in propellant.

Influence of Substitution of Lead Salicylate by Nitrophenylazo Groups in the 5 Position. A phenolic hydroxyl group is subject to tautomeric influences which may enable this group to exist in the form of a carbonyl group. This influence was studied by introduction of an azo group in the para position to the hydroxyl group. This introduction produces a ketoenol-like equilibrium between a quinone-hydrazone form and the phenol-azo form. A para nitrophenylazo group was used to study the influence of a complete quinonehydrazone form involving two aromatic nuclei. The limitation of this form to one nucleus was studied with the help of the m-nitrophenylazo compound, the lead salt of which has a yellow-orange color whereas the para-compound gives a lead salt of red color. Only the tautomeric quinone hydrazone forms are shown.



18. Lead salt of 5-(3-nitrophenylazo)-salicylic acid. Alizarin Yellow G. (Lead salt orange)



19. Lead salt of 5-(4-nitrophenylazo)-salicylic acid. Alizarin Yellow R. (Lead salt red)

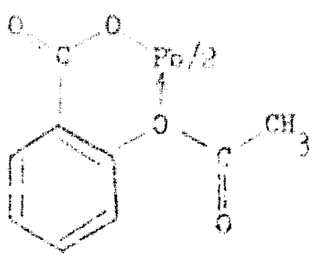
TABLE 14. Influence of Quinone Hydrazone Formation Possibilities on "Modifier Effectivity"

Characteristics	18. Pb salt of 5-(3-nitrophenyl-azo) salicylic acid	19. Pb salt of 5-(4-nitrophenyl-azo) salicylic acid	17. Pb 5-tertiary-butyl-salicylate
Modifier effectivity ..	69	46	193
Superrate area .	69	55	195
Pb compound by analysis, % ..	4.0	4.6	2.9
Pb in compound, %	26.57	26.57	34.92
Pb in propellant, %	1.0	1.2	1.01
Heat of explosion of propellant, cal/g	854	852	842
PL Mc	614	615	683

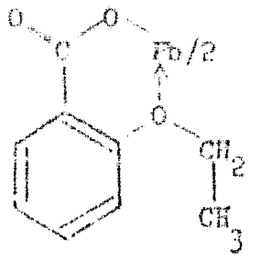
The results in Table 14 show that increasing possibilities of quinone-hydrazone formation gradually decrease "modifier effectivity" in contrast to a substitution of the 5 position by an alkyl group.

Influences of Substitution of the Hydroxyl Group in Lead Monohydroxybenzoates. The question of whether or not a modification of the hydroxyl group might influence the activity was also of

interest. Therefore, the data of acetylation and ethylation products were compared with the original compounds as Table 15 shows.



20. Lead acetylsalicylate



21. Lead 2-ethylbenzoate

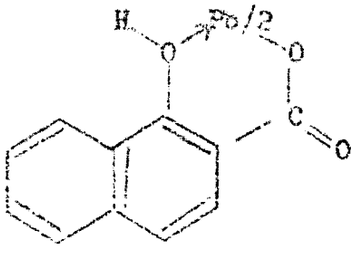
TABLE 15. Influence of Substitution of the Hydroxyl Group in Lead Salicylate

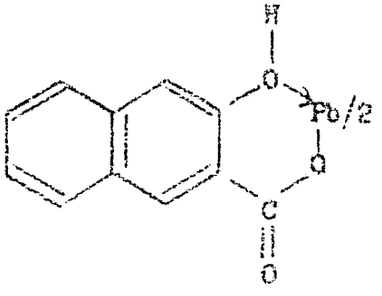
Characteristics	High heat of explosion		Low heat of explosion		
	20. Pb acetyl-salicy-late	13. Pb salicy-late	21. Pb 2-eth-oxyben-oate	2. Pb salicy-late	1. Pb 2-ethyl-hexano-ate
Modifier effectivity	123	156	149	291	66
Superrate area	95	195	120	250	44
Pb compound by analysis, %	2.1	2.9	2.0	2.0	1.6
Pb in compound, % ..	36.64	43.04	40.67	43.04	41.98
Pb in propellant, %	0.77	1.25	0.81	0.86	0.67
Heat of explosion of propellant, cal/g	929	868	747	770	784
PL No	174	227	385	120	121

Comparing lead acetylsalicylate and salicylate, one must observe that the heat of explosion of the acetylsalicylate composition is somewhat higher, which condition reduces its effectivity to some extent. Considering this, the effects of the two compounds appear very similar. The reason for such behavior is probably the ease with which the ortho-acetoxy group is hydrolyzed. The ethoxy group is much more stable, and the effectivity falls to about 50% of the value for the salicylate. It is, however, considerably higher than that for lead 2-ethylhexanoate probably because of the higher reactivity of the

aromatic system and its ability to form a bidentate group. The superrates of both lead 3- and 4-hydroxybenzoates (Table 8) cease upon acetylation or alkylation of these groups (Ref. 9).

Influences of Lead Salts of Polynuclear Aromatic Hydroxy-Carboxylic Acids With Reactive Ortho or Para Positions. All previous discussions about carboxylic acids were grouped around salicylates and their substitution products and isomers. It was, therefore, of interest to find out whether ortho hydroxy carboxylic acids of other aromatic systems followed the same general rules. The hydroxy lead naphthoates offered the possibility for such a comparison. (See Table 16).





22. Lead 1-hydroxy-2-naphthoate 23. Lead 2-hydroxy-2-naphthoate

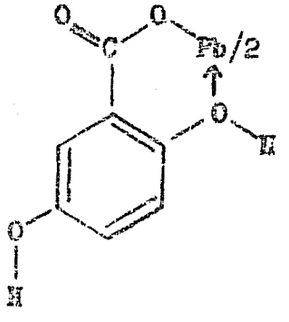
TABLE 16. Influence of Polynuclear Hydroxy Carboxylic Acids with Reactive Ortho or Para Positions

Characteristics	22. Pb 1-hydroxy-2-naphthoate	23. Pb 2-hydroxy-3-naphthoate	13. Pb salicylate	16. Pb o-cresotinate
Modifier effectivity	164	160	156	97
Superrate area	164	176	195	126
Pb compound by analysis, %	2.9	3.3	2.9	3.2
Pb in compound, % ..	35.63	35.63	43.04	40.64
Pb in propellant, %	1.0	1.0	1.25	1.3
Heat of explosion of propellant, cal/g	846	867	868	748
PL No	611	492	227	486

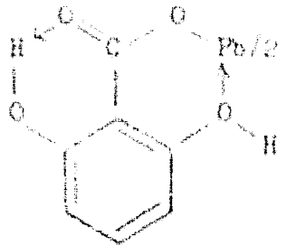
The results of this comparison show that these compounds have almost the same effectivity as that of lead salicylate and exceed that of lead o-cresotinate. For lead 2-hydroxy-3-naphthoate, this superiority can be easily understood since a position ortho to the hydroxyl group is available in the same nucleus. The lead 1-hydroxy-2-naphthoate does not have such an ortho position available. It should, for this reason, act similarly to lead o-cresotinate. In an earlier paragraph, the smaller "modifier effectivity" of this last compound has been related to the substitution of the ortho position of the hydroxyl group by a methyl group. The difference between the results of these two compounds may be caused by the fact that the 4 position in 1-hydroxy-naphthalene is more reactive than the 4 position in a phenol molecule, the former being an alpha position in a naphthalene nucleus (Ref. 14).

Influence of Lead Di- and Tri-hydroxybenzoates as Additives. The previous discussion of the influence of lead salicylate and related compounds had shown that any influence which reduces the reactivity of the organic portion of the compound in a position ortho to the aromatic hydroxyl or other equivalent group also reduces the "modifier effectivity" in double-base propellant burning. It remained of interest to find out whether differences in the position of a second hydroxyl group would give similar results. The effects on the burning rate diagrams obtained with such products differed to a considerable extent from the plateau and mesa effects of the previously investigated products. The general form of these diagrams was plateau in character and not mesa-like. However, they could be extended to higher ranges of heats of explosion, burning rates, and pressures, than the diagrams for lead aliphatics or lead salicylate modified propellants (see Fig. 1).

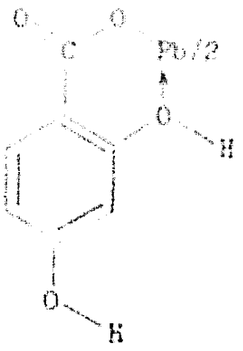
Investigation of these lead salts of dihydroxy carboxylic acids in double-base propellants showed that the total increases in "modifier effectivities" were very significant. These effects are shown in Table 17.



24. Lead 2,5-dihydroxybenzoate (Lead gentisate)



25. Lead 2,6-dihydroxybenzoate
(Lead Y-resorcylate)



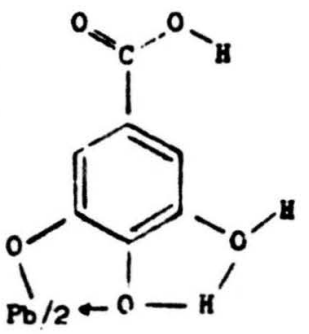
26. Lead 2,4-dihydroxybenzoate
(Lead β-resorcylate)

TABLE 17. Influence of Dihydroxybenzoic Acids

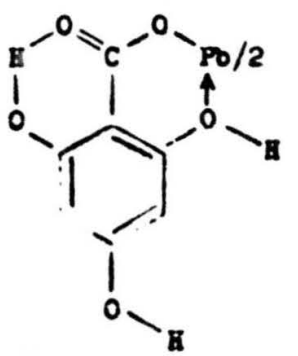
Characteristics	13. Pb salicylate	24. Pb gentisate	25. Pb Y-resorcylate	26. Pb β-resorcylate
Modifier effectivity	156	292	347	382
Superrate area	195	342	298	340
Pb compound by analysis, %	2.9	2.29	2.12	2.2
Pb in compound, %	43.04	40.36	40.36	40.36
Pb in propellant, %	1.25	1.17	0.86	0.89
Heat of explosion of propellant, cal/g	868	853	847	839
PL No	227	493	Ref.15	392

All lead dihydroxybenzoates have considerably higher "modifier effectivities" than lead salicylate. The differences among the dihydroxy compounds themselves are much smaller. Lead gentisate has 187%, lead Y-resorcylate 222%, and lead β-resorcylate 245% of the "modifier effectivity" of lead salicylate. The fact that the hydroxyl groups in lead gentisate are para to one another is in line with this somewhat smaller increase in "modifier effectivity". Two hydroxyl groups in meta position to each other support their individual influences to a higher degree as is demonstrated by the larger modifier effectivities of lead Y- and β-resorcylate.

The above results seemed to require a further extension of the investigations to include trihydroxybenzoates. For this purpose, lead gallate was investigated at NOTS and lead phloroglucinol carboxylate at the Ordnance Missile Laboratories of the Army at Redstone Arsenal (Ref. 16). The results are shown in Table 18.



27. Lead 3,4,5-trihydroxybenzoate (Lead gallate)



28. Lead 2,4,6-trihydroxybenzoate (Lead phloroglucinol carboxylate)

TABLE 18. Influence of Trihydroxybenzoic Acids

Characteristics	27. Pb gallate	28.[a]	13. Pb salicylate	26. Pb resorcylate	5. Pb catecholate
Modifier effectivity	251	....	156	382	26
Superrate area	294	....	195	340	49
Pb compound by analysis, %	3.1	....	2.9	2.2	2.9
Pb in compound, % ..	37.99	....	43.04	40.36	65.72
Pb in propellant, %	1.17	...	1.25	0.89	1.90
Heat of explosion of propellant, cal/g	873	....	868	869	863
PL No	610	Ref. 16	227	392	644

[a] No burning-rate-modifying effects were observed for No. 28, Pb phloroglucinol carboxylate.

Lead gallate has a considerably higher "modifier effectivity" than lead salicylate (160.4%) but only two-thirds of

the effect of lead β-resorcylate (65.7%). The formation of the most effective, salicylate-type of bidentate group is, of course, not possible in lead gallate. The formation of a less effective lead catecholate type coordination is, however, possible and has been proven for the iron complexes used in permanent inks (Ref. 17). Similar observations have been made with metal compounds of 5-sulfo-8-hydroxyquinolinates (Ref. 18). Lead gallate contains a third hydroxyl group which is not involved in this salt formation. This may explain the higher reactivity of this compound compared to lead catecholate.

The fact that no burning rate modifying effects at all were observed with lead phloroglucinol carboxylate may be due to the very low thermal stability of this acid which may have caused its decomposition before it entered the reaction zone. Table 19 shows the melting points and temperatures of decomposition for some polyhydroxybenzoic acids.

TABLE 19. Melting and Decomposition Points of Investigated Polyhydroxybenzoic Acids

Acid	Melting point, °C	Decomposition point, °C
α-resorcylic	232-3	above 237
Gallic	222	222
β-resorcylic	213	above melting
Gentisic	200	215
γ-resorcylic	148-167	148-167
Phloroglucinol carboxylic ..	no melting below decomposition	100

Influences of Substitution of Hydroxyl Groups in Lead β-resorcylate. The amount of influence of the hydroxyl groups in lead β-resorcylate has been tested by observing the changes obtained through acetylation and ethylation of such groups. The results are shown in Table 20. These data indicate that the highest "modifier effectivities" are obtained if both hydroxyl groups are free.

Table 21 gives a comparison of the relative "modifier effectivities" (r) of these compounds compared to lead salicylate as unity.

TABLE 20. Influence of Hydroxyl Group Substitution in Lead β-resorcylate

Characteristics	26. Pb β-resorcylate[a]	29. Pb 2,4-diacetoxybenzoate	30. Pb 2-hydroxy-4-acetoxybenzoate	31. Pb 2-hydroxy-4-ethoxybenzoate	1?. Pb salicylate	20. Pb acetylsalicylate
Modifier effectivity	382	136	106	71	156	123
Superrate area	340	112	106	46	195	95
Pb compound by analysis, %	2.2	2.7	2.9	1.8	2.9	2.1
Pb in compound, %	40.36	30.4	34.68	36.38	43.04	36.64
Pb in propellant, %	0.89	0.82	1.00	0.65	1.25	0.77
Heat of explosion of propellant, cal/g	839	843	854	862	868	929
PL No	392	643	598	510	227	174

[a] Lead 2,4-dihydroxybenzoate.

TABLE 21. Relative "Modifier Effectivities" (r) of Lead 2,4-dihydroxybenzoate and its Acetylation and Alkylation Products

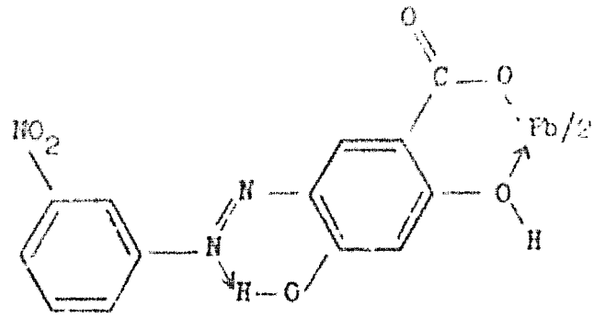
Lead compounds	(r)	PL No.
a. Lead salicylate	1.00	227
b. Lead 2,4-dihydroxybenzoate	2.45	392
c. Lead 2-hydroxy-4-acetoxybenzoate ..	.68	596
d. Lead 2-hydroxy-4-ethoxybenzoate ...	.46	510
e. Lead 2,4-diacetoxybenzoate	.87	643
f. Lead acetylsalicylate	.79	174

Since the 4-hydroxyl group is not part of a bidentate group, acetylation or alkylation of this group was not expected to appreciably change the "modifier effectivity". However, the corresponding "modifier effectivities" of (c) and (d) are even below the value for lead salicylate (a). The modifier effectivity of lead 2,4-diacetoxybenzoate (e) is, surprisingly, slightly better than the value of lead 2-hydroxy-4-acetoxybenzoate (c). It compares fairly well with the "modifier effectivity" of lead acetylsalicylate (f), when the proper allowances are made for differences in heat of explosion.

It had been expected that such derivatives of lead salicylate not having the possibilities of quinone formation or increased intramolecular resonance would give "modifier effectivities" higher than that of lead salicylate. Because of the contradicting results, the possibility of the acetylation or alkylation having occurred at the bidentate hydroxyl group was considered. This, however, does not appear probable from the work published on this subject. The possibility that steric influences from the substituent in the 4 position may hinder the reactivity of the 3 and 5 positions of this compound has been discussed to explain such behavior but cannot be supported by any other related experiences. Additional investigations would be necessary to clarify this situation, inasmuch as the actual reaction mechanism may be based on more involved relationships than reactivities and presence of bidentate groups in these compounds.

The effects of exchanging the 5-alkyl group in lead 5-tertiary-butylsalicylate by 5-nitrophenylazo groups were shown in Table 13. These exchanges reduced the "modifier effectivity" of the compound considerably. The same was the case with the β-resorcylate

derivatives. Furthermore, hydrogen bonding will be obtained between the 4 hydroxy group and the azo group, as the following structural formula shows:



32. Lead salt of 5-(3-nitrophenylazo) β-resorcylic acid (Lead 5-(m-nitrophenylazo) β-resorcylate)

TABLE 22. Introduction of Nitrophenylazo Groups in the 5 Position to Lead β-resorcylate

Characteristics	32. Pb 5-(m-nitrohpenylazo) β-resorcylate	18. Pb salt of 5-(3-nitrophenylazo)-salicylic acid	26. Pb β-resorcylate
Modifier effectivity	94	69	382
Superrate area	74	69	340
Pb compound by analysis, %	3.0	4.0	2.2
Pb in compound, %	26.37	26.57	40.36
Pb in propellant, %	0.89	1.00	0.89
Heat of explosion of propellant, cal/g	868	854	839
PL No	722	614	392

The data in Table 22 show a 75% reduction of the "modifier effectivity" from introduction of the m-nitrophenylazo group in the 5 position of lead β-resorcylate whereas in the case of the

salicylate derivative, compound 18, the "modifier effectivity" dropped by 56%. The effect of the second hydroxyl group is, therefore, considerably reduced in compound 32 probably because of the intramolecular neutralization of the effects of the hydroxyl group as shown by the structure.

CONCLUSIONS

The quotient of the "superrate area" divided by the lead content of burning-rate-modifying agents has been called "modifier effectivity". Use of these effectivities allows, at comparable levels of heat of explosion, an evaluation of the constitutional influence of the organic part of such agents. In many cases, certain chemical relationships between chemical structure and "modifier effectivity" were established. The presence of a bidentate group including one carboxyl, carbonyl, or equivalent group and one phenolic hydroxyl or equivalent group produces large "modifier effectivities". Still larger effects are obtained from similar aromatic compounds with two hydroxyl groups even without vicinal positioning of any of the substituents. The aromatic part of the molecule should have the possibility of reacting easily under nucleophilic substituting influences, as proposed in Ref. 4, and positions for such reactions should not be substituted by organic groups. The substituents of such molecules should not saturate each other completely by intramolecular influences but should allow for a high degree of interaction with the surrounding propellant matrix in the early zones of the progressing combustion wave.

The importance of bidentate groups including a carboxyl, carbonyl, or equivalent group and a phenolic hydroxyl or equivalent group for the formation of highly active lead compounds, considered with the small influence of variations in dissociation constants, seems to suggest that the lead atoms in some of these compounds may not be present in ionic form but in the form of chelate complexes. The observations made in Ref. 4 about relationships between certain radiation absorbing additives and changes in superrate burning effects may also be valid for the "modifier effectivities" of the compounds discussed in this report. It appears possible that compounds containing bidentate groups may react with other lead compounds in the propellant matrix to form the actual burning rate modifying agents. This may also be indicated by the results of the investigations of the recently published Ref 19. An extension of the investigations of Ref. 18 directed to ascertaining the actual form of the lead compound within the propellant matrix would seem valuable for the further development of these agents. The application of general principles of

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their interaction might be helpful for the development of similarly acting additives for other solid propellant or liquid monopropellant systems.

[redacted]

REFERENCES

1. Solid Propellant Information Agency, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland. Tenth Meeting of the JANAF Solid Propellant Group, Wright Air Development Center, Dayton, Ohio, June 2, 3, 4, 1954, Vol. I. "Possible Catalytic Mechanisms in Double Base Propellant Burning", by A. T. Camp, C. H. Carlton, and H. K. Haussmann, USNOTS, pp. 81-108, CONFIDENTIAL.

2. Carlton, C. H. An Interpretation for Catalytic Burning of Mesa Propellants, Memorandum Reg. 4521028, USNOTS, 13 July 1953, CONFIDENTIAL.

3. U. S. Naval Ordnance Test Station, China Lake. Equilibrium Composition and Thermodynamic Properties of Combustion Gases, Part 4, Theoretical Product Compositions, Equilibrium, Thermodynamic Functions, and Performance Data of N-4, N-5, and X-6, by William S. McEvan and Mary M. Williams. China Lake, Calif., NOTS, 16 March 1953. (NAVORD Report 1229, NOTS 671), CONFIDENTIAL.

4. ---- . A Decade of Progress in the Understanding of Certain Ballistic Properties in Double-Base Propellants, by A. T. Camp, H. K. Haussmann, W. S. McEvan, H. A. Henry, R. H. Olds, and E. D. Besser. China Lake, Calif., NOTS, 21 January 1958. (NAVORD Report 5824, NOTS 1914), CONFIDENTIAL. AD-[illegible]

5. Hercules Powder Company, Allegany Ballistics Laboratory. Strand Rate Ballistic Studies of Plateau-Type Propellants, Part IV. Characteristics of Various Ballistic Modifiers, by J. H. Godsey and R. F. Preckel. Cumberland, Maryland, April 1955. (Report ABL/P-25), CONFIDENTIAL.

6. Noyes, A. A. and W. H. Whitcomb. The Solubility of Lead Sulfate in Ammonium Acetate Solutions, J AM CHEM SOC, Vol. 27 (June 1905), p. 756.

7. Conrad, W. Beiträge zum Electrochemischen Verhalten des Bleis, Dissertation University of Goettingen, 1903.

8. Abegg, R. Zur Kenntins der Konstitution von Salzloesungen, Zeitschrift fur Electrochemie, Vol. 10 (January 1904), p. 78.

9. Hercules Powder Company, Allegany Ballistics Laboratory. Monthly Progress Report No. 2, December 1951, Cumberland, Maryland, CONFIDENTIAL.

10. Pauling, Linus. The Nature of the Chemical Bond and the Structure of Molecules and Crystals, 2nd ed. Ithaca, New York, Cornell University Press, 1945.

11. Hercules Powder Company, Allegany Ballistics Laboratory, Technical Department Weekly Progress Report 210, February 8, 1950. Cumberland, Maryland, CONFIDENTIAL.

12. Abell, R. D. Derivatives of Phenyl Styryl Ketone, J CHEM SOC (London), Vol. 101, 1912, p. 998.

13. Hammett, Louis P. Physical Organic Chemistry. New York, McGraw-Hill, 1940, p. 35.

14. Branch, G. E. K., M. Calvin. The Theory of Organic Chemistry. New York, Prentiss Hall, March 1947, p. 485.

15. U. S. Naval Ordnance Test Station, Inyokern. Research in Chemistry, by the Chemistry Division. China Lake, Calif., NOTS, 31 January 1955. (NAVORD Report 3422, NOTS 1021), CONFIDENTIAL.

16. Redstone Arsenal. Monthly Report for Rocket Development Laboratory, Rocket Development Division, Huntsville, Ala., Redstone, 30 June 1954. (3M7M3), CONFIDENTIAL.

17. Silberman, T. and N. Ozorovitz. The Ability of Gallic Acid and Related Substances to Form Complex Salts, Chemical Abstracts, Vol. 2 (1908), p. 2685.

18. Martell, Arthur Earl and Melvin Calvin. Chemistry of the Metal Chelate Compounds. New York, Prentiss Hall, 1952. p. 50.

19. Hercules Powder Company, Allegany Ballistics Laboratory. Strand Rate Ballistic Studies of Plateau-Type Propellants, Part V. Characteristics of Various Ballistic Modifiers, by J. H. Godsey. Cumberland, Maryland, November 1958. (Report ABL/P-37), CONFIDENTIAL. 304221